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EXTRACT FROM OAK BARK USED AS AN ANTIBACTERIAL COLOURANT FOR POLYAMIDE TEXTILES

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ABSTRACT

The aim of this study was to test properties of the polyamide fabrics dyed using extract from oak bark that is a rich source of hydrolysable tannins. Tested were: optimal conditions for water extraction, light and wash fastness, health safety and antibacterial properties for use of clothing with sweat and bacteria exposed areas, such as socks. The results showed that all samples also met the strict requirements for children's clothing.

KEYWORDS: Polyamide fabric, oak bark, tannin, antibacterial, fastness, natural dyes.

INTRODUCTION:

Natural dyes are becoming the object of scientific interest even in the countries where their use does not have a strong tradition. It is generally caused by the growing trend of returning back to nature and to natural products. Some plant extracts combine the properties of natural dyes and herbal remedies, so the finished product has not only the properties of the dyed fabric but also healing and antiseptic properties. Frequently applied in natural dyeing, are extracts from plants that are a mixture of different substances in which tannins (omnipresent vegetable tanning agents) often play an important role.

Oak bark is a rich source of tannins (water soluble polyphenols) that can to coagulate proteins and form complexes with metals that have a number of biogenic effects. Contained here are not only the hydrolysable tannins (gallotannin, tannic acid, ellagitannins) [1] but also condensed tannins (proanthocyanidins) [2,3], catechin, epicatechin [4], and other substances such as cellulose, hemicellulose, lignin and others [5].

The oak bark extract is used in folk medicine for its antiseptic properties and its ability to inhibit and stop bleeding. Its healing properties are used for example in the treatment of haemorrhoids, skin inflammation, smaller burns and excessive perspiration of the feet. Oak bark exhibits these medicinal effects due to tannins that have strong astringent properties. Tannins have the ability to coagulate proteins thereby reducing vascular permeability and cell and tissue secretion [6]. The antibacterial effect of tannins is described as well [7]. The inhibitory effect on bacterial enzymes occurs due to the ability of tannins to coagulate the proteins and to form complexes with metals. This ability also allows for direct binding to protein receptors on the surface of bacterial membranes and depriving the essential micronutrients required for a microbial growth, such as iron or zinc [8].

Tannins have always been used on textiles as a treatment to increase wash and light fastness, mainly on cotton fabrics. Although the mechanism of the fixative effect on dyes is not fully understood, the ability of tannins to form complexes with certain substances, including dyes, is widely used [9]. Tannins have a strong affinity to the polyamide that is used e. g. for the purification of vegetable extracts (tannin removal) with polyamides. Furthermore, tannins are used in the food industry to alter fruit juices (the removal of tannins eliminates their bitterness) [10]. We took advantage of this natural affinity of tannins to the polyamide and used the oak bark extract that is a rich source of tannins and other phenolic compounds to dye polyamide fabric. It was dyed in a dyeing bath and the finished product was subsequently tested for wash fastness, light fastness, antibacterial properties and the health safety.

MATERIALS AND CHEMICALS:

Materials: Mixture of dried crushed oak bark from trees English oak (Quercus robur), sessile oak (Quercus petraea) and downy oak (Quercus pubescens), polyamide 6.6 fabric (PA, surface weight of 78 g m^{-2}), Petri dishes with universal culture soil TSA (Tryptone Soya Agar), inoculum of Gram-negative bacteria *Escherichia coli* and inoculum of Gram-positive bacteria *Streptococcus gallinarium* in TSB (Tryptone Soya Broth) medium.

Chemicals: Sodium carbonate anhydrous (Na_2CO_3), Folin-Ciocalteau reagent, L–histidine monohydrochloride monohydrate ($C_6H_9O_2N_3.HCl.H_2O$), sodium chloride (NaCl), disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4.12H_2O$), sodium hydroxide (NaOH), sodium dihydrogen phosphate dihydrate ($NaH_2PO_4.2H_2O$).

METHODS:

Extraction and dyeing:

Tannins from oak bark were extracted by water in stainless steel cartridges of the apparatus known as Ahiba with controlled heating and the optional rotation of cartridges. Crushed oak bark is a hard and difficult material to extract from; therefore, it is necessary to choose longer extraction times. Because of the fact that the absorption spectrum of the oak bark extract showed no significant maximum in visible light **(Figure 1)**. The yield of the extract was measured by a method for determination of phenolic groups using the Folin reagent. The following was pipetted into a test tube: 1 ml of diluted folinic agent, 1 ml of distilled water, 50 microlitres of the sample and 1 ml of sodium carbonate solution. Samples were measured in a spectro- photometer at a wavelength of 736 nm after 45 minutes of incubation. Items tested were various extraction times, different temperatures and the weight ratio of extracted material and extraction bath.

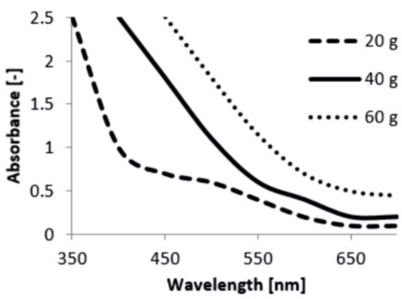

Figure 1: Absorption spectra of the extracts of oak bark (spectrophotometer UV-1600 PC Mapada, China)

Antibacterial tests:

The antibacterial properties of the polyamide fabric dyed with the oak bark extract at a concentration of 60 g L^{-1} of water were tested using Gram-negative bacteria *Escherichia coli* and Gram-positive bacteria *Streptococcus gallinarum*. The concentration of 10^4 CFU in 1 ml of suspension was prepared by the dilution of the original inoculum in TSB using a sterile saline solution. The dyed polyamide fabric (0.5 g) and undyed polyamide fabrics (blanks, undyed natural samples that were cooked for one hour only in a water bath) were placed in closed tubes with 10 ml of the inoculum at a concentration of 10^4 CFU in 1 ml. The treated samples were left for 4 and 24 hours in dynamic contact and gently agitated using an oscillating shaker at room temperature. After 4 and 24 hours the fabrics were transferred into 30 ml of the sterile saline solution. The suspensions (1 ml of each) were collected for cultivation on TSA after vigorous shaking of the tubes for 5 minutes. The cultivation was carried out in an incubator at 37 °C for 24 hours. The numbers of grown colonies were then counted and their decrease in percentage was calculated in relation to the undyed blank.

Another antibacterial test was carried out with fabrics that have been washed after dyeing in 1, 2 or 3 wash cycles, each lasting 30 minutes. Dyed fabrics and undyed blanks (0.5 g samples) were exposed to dynamic contact with 10 ml of bacterial inoculum of *E. coli* or *S. gallinarum* (concentration 10^4 CFU in 1 ml) for 8 hours at 37 °C. Then all samples were strongly shaken in 10 ml of the sterile saline solution and 1 ml of each suspension was collected for cultivation on TSA.

After 24 hours of the incubation at 37 °C the CFU grow was counted and expressed as a percentage in relation to the blank.

Wash fastness:
The wash fastness was done by a modified procedure based on the standard EN ISO 105 - a01 (80 0120) - Textiles - Tests for colour fastness - Part A01: General principles of testing. The so-called compound sample is tested by this standard: the sample 10 x 4 cm is composed of three layers of fabric (the first accompanying undyed polyamide fabric, the second accompanying undyed wool fabric and the dyed fabric). The compound sample was inserted into rotary cartridges of the dyeing apparatus and washed in the thermostatically controlled water bath of 40 °C with the addition of liquid detergent without optical brighteners, enzymes and without pH modification (alkalinisation). The detergent was administered as 20 ml per litre of wash bath; washing took place at a length of bath of 1:50 for 60 minutes in distilled water in mode for washing delicate fabrics (1 rpm). After separate drying, the colour change of the dyed fabric was evaluated with the colour absorption of the accompanying fabric. The objective measurements for shade changes were obtained using the L* a* b* values from the CIE-Lab colour space (L_1*, a_1*, b_1* are the original values, L_2*, a_2* and b_2* are the values after irradiation), *ΔE* (colour deviations) were calculated according to the formula (1) and converted to the grey scale [11]. Degree 5 of the grey scale represents the minimum colour deviation, which means the maximum stability. Degree 1 represents a big change in the hue and therefore the worst degree of fastness.

$$\Delta E = \sqrt{(L_2{*} - L_1{*})^2 + (a_2{*} - a_1{*})^2 + (b_2{*} - b_1{*})^2} \quad (1)$$

Light fastness:
The light fastness was tested by high pressure discharge lamps Ultramed 400 (Osram) with an output of 8.18 Wm^{-2} in UVA and 1.71 Wm^{-2} in UVB radiation. Using the blue scale for light fastness of wool textiles it has been found that two hours of this exposure corresponds to a distortion of degree 2, four hours of exposure corresponds to degree 3 and after seven hours of exposure degree 4 of the blue scale is distorted. The blue light fastness scale is a range of eight blue dyeings on the woollen fabric where a following dye decomposes 2 or 4 times slower than the previous one. The degree 1 means the worst light fastness, degrees 6-7 represent excellent levels of light fastness.

Health safety:
The Decree of the Ministry of Health on hygiene requirements for toys and products for children up to 3 years of age [12] contained in Annex no. 10, Clause 2, states that the pH of the leaches shall not exceed limit of 4.0 to 7.5. Leaches were obtained by shaking 2 g of textiles in 100 ml of distilled water for 2 hours at room temperature (20 ± 2) °C. This Decree also contains provisions (in Annex 10, paragraph 5 and 6) on the content of hazardous elements in extracts simulating acid and alkaline perspiration. To determine the extracted metals, 2 g of fabrics were leached in 100 ml of solutions simulating acidic and alkaline sweat at 37 °C for 4 hours. Subsequently, the fabrics were removed from solutions and leaches were analysed by ICP-OES device Perkin Elmer Optima 2100. Some elements (Pb, Ni, Co) were measured on the device with lower detection limits (ICP-MS Perkin Elmer NexIon 300D). The composition of the fluid simulating the alkaline sweat: 0.5 g of L–histidine monohydrochloride monohydrate, 5.0 g of sodium chloride, 5.0 g of disodium hydrogen phosphate dodecahydrate, the pH of the solution is adjusted to 8.0 with a sodium hydroxide solution with a concentration of 0.1 mol L^{-1}.

The composition of the fluid simulating acid sweat: 0.5 g of L–histidine monohydrochloride monohydrate, 5.0 g of sodium chloride, 2.2 g of sodium dihydrogen phosphate dihydrate, the pH of the solution is adjusted to 5.5 with sodium hydroxide solution with a concentration of 0.1 mol L^{-1}.

RESULTS AND DISCUSSION:

Extraction and dyeing:
The optimum extraction temperature of 100 °C for 60 minutes using the extraction rate of 60 g of the oak bark per 1 litre of water was selected by evaluation of graphs in **Figures 2, 3** and **4**. To simplify the whole process, dyeing was carried out simultaneously with extraction in the ratio of 1 : 50 : 4, 2 or 1 (1 g of PA fabric : 50 ml of extraction/dyeing bath : 4, 2 or 1 g of dried oak bark depending on the density of the final hue). The extraction-dyeing mode was as follows: After 20 minutes, the extraction/dyeing bath reached a maximum temperature (95 °C). Spontaneous cooling of the bath occurred after one hour. Dyeing and extraction were carried out with the rotation of cartridges at 20 rpm. After dyeing the fabrics were washed thoroughly in water and dried.

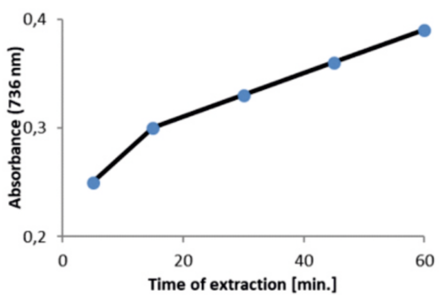

Figure 2: The increase in absorbance of the oak bark extract after reaction with Folin reagent depending on prolonged time of extraction (80 °C, 60 g L^{-1})

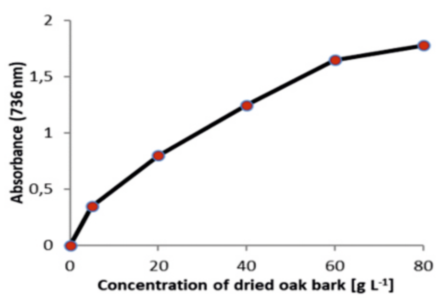

Figure 3: The increase in absorbance of the oak bark extract after reaction with Folin reagent depending on increased amount of extracted material in bath (80 °C)

The fabrics were dyed in three different intensities of colour with three concentrations of oak bark in the bath, namely 20, 40 and 80 g of oak bark per 1 litre of water.

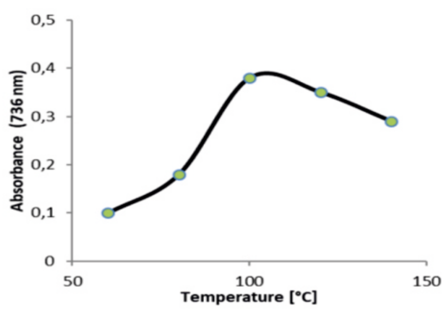

Figure 4:The increase in absorbance of the oak bark extract after reaction with Folin reagent depending on increased temperature (80 °C, 60 g L^{-1}, each extraction 60 min.)

Table 1 contains L* a* b* values of dyed fabrics and the fastness results.

Table 1: The L*a*b* values and fastnesses of fabrics dyed by oak bark in 3 different densities

Concentration of oak bark [g L^{-1}]	L*	a*	b*	Wash fastness[1]	Light fastness[2]
80	62.4	11.8	16.1	4 - 5	> 4
40	65.5	10.9	13.2	4 - 5	> 4
20	72.4	8.2	10.4	4 - 5	> 4

Notes: [1] degrees of grey scale
[2] degrees of blue scale

As seen in **Table 1**, all samples exhibited very good wash fastness (grade 4-5 of the grey scale) and very good light fastness (exceeding grade 4 of the blue scale). Those were expected results as tannins were used to improve fastness of dyed fabrics as a pre- or post-treatment.

Antibacterial properties:
Table 2 contains the reduction in the CFU number in dyed fabrics with relation to a control sample that grew on TSA. The significant decrease in the number of CFU was in the contact with both bacteria species that confirmed the antibacterial ability of the oak bark extract.

Table 2: Number of bacteria (CFU) after contact with dyed fabrics in comparison with undyed control samples

Bacteria	0 h	4 h	24 h
Escherichia coli	100%	71%	60%
Streptococcus gallinarum	100%	88%	60%

Table 3 shows that the dyed fabric maintained an antibacterial capability even after three wash cycles. It was tested in contact with a bacterial concentration of 4 x 10^3 CFU in 1 ml for 8 hours at 37 °C.

Table 3: The number of bacteria (CFU) after contact with washed dyed fabrics in comparison with washed undyed control samples

Bacteria	Without washing	1 wash cycle	2 wash cycles	3 wash cycles
Escherichia coli	15%	18%	30%	56%
Streptococcus gallinarum	4%	8%	20%	36%

Health safety:
The oak bark extract itself had a pH of 4.95 and the extract of polyamide fabric dyed by this extract (PA / oak) had a pH of 5.9. That meets the prescribed range of specified pH leaches.

Values of leached metals were converted to kilogram of leached fabric. The content of metal in the oak bark extract is shown as the kilogram of the dried oak bark extracted by boiling for 1 hour. The metal concentration in solution (mgL^{-1}) is shown directly in the distilled water, alkaline and acid sweat.

As concluded from **Table 4** and its comparison with the limits on the second line, no content of leach from the fabric did exceed metals limit specified by [12] for the health safety products for children up to 3 years.

Table 4: Metal content in the test leaches

Item	Ni [mg/kg]	Pb [mg/kg]	Cr [mg/kg]	Cu [mg/kg]	Co [mg/kg]	Al [mg/kg]	Cd [mg/kg]
Limit [mg kg^{-1}][3]	max. 1.0	max. 0.2	max. 1.0	max. 25.0	max. 1.0	no limit	max. 0.1
Distilled water	<0.01	<0.00001	<0.002	0.03	<0.01	<0.01	<0.002
Extract from oak [4]	0.445	0.036	0.19	<1.0	0.028	2.6	0.006
Alkaline sweat	0.002	0.0001	0.017	0.01	0.0005	0.024	$0.04.10^{-3}$
PA in alkaline sweat	0.116	0.038	0.88	0.71	0.025	0.57	0.004
PA/oak in alkaline sweat	0.112	0.009	0.88	0.58	0.028	0.88	0.002
Acid sweat	0.004	0.0007	0.018	0.12	0.0002	0.016	$0.06.10^{-3}$
PA in acid sweat	0.206	0.067	0.93	5.57	0.011	1.05	0.005
PA/oak in acid sweat	0.245	0.003	0.84	5.79	0.013	0.69	0.004

Notes: [3] limits of metal leached in the acid and alkaline sweat (related to 1 kg of fabrics) that cannot be exceeded according to [12]
[4] based on 1 kg of dried oak bark.

CONCLUSIONS:
The polyamide fabric was dyed with the oak bark extract to a shade of brown colour in 3 different densities. Those have shown excellent wash fastness (degrees 4-5 of grey scale) and very good light fastness (more than the degree 4 of the blue scale). The treated fabric showed partial and significant antibacterial effect after 4 and 24 hours of contact with bacteria Escherichia coli and *Streptococcus gallinarum* that occurred in dyed fabrics after shaking in physiological saline solution to a decrease of CFU growth down to 60 % compared with the undyed polyamide fabric. The significant antibacterial effect remained even after three wash cycles.

Leaches from dyed fabrics also met strict requirements for the health safety, because their pH and the metal content did not exceed values of the Decree [12] about health and safety products for children up to 3 years.

We have demonstrated that polyamide fabric dyed with the oak bark extract combines all the expected qualities. The great affinity to the polyamide fibre became apparent from very good wash and light fastness, and antibacterial properties partially preserved in tested fabric even after three wash cycles. The polyamide fabric dyed with the oak bark extract is a very suitable material for clothing with sweat and bacteria exposed areas, such as socks, and thanks to its health safety it is also suitable for baby clothes.

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